



Dechlorination of chlorobenzene compounds on flyash; effects of metals, aqueous/organic solvents and temperatures

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ABSTRACT

Dechlorination of chlorobenzene compounds on flyash by using a solution of calcium hydroxide and sulfur in aqueous/organic solvent at 60–170 °C, under oxygen deficient conditions was studied. High percentage of dechlorination was obtained under certain reaction conditions. The results suggested that at 90 °C, metals in general and copper and lead in particular enhanced the catalytic potential of flyash for dechlorination by hydrodechlorination and substitution reactions. But at high temperatures (120–170 °C), dechlorination process was adversely affected by these metals. The effects of water, organic solvents, temperatures and heating time, were studied and reactions conditions were optimized to get maximum dechlorination.

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1. Introduction

Chlorinated organic compounds are widely used in the chemical and electronic industries. Disposal of chlorinated organic wastes in such a way as to minimize the environmental hazards has become an urgent issue. Conventional incineration of these wastes produces harmful compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), unless the operating temperature is strictly controlled [1]. Many methods for the dechlorination of chlorobenzene compounds have been consequently developed. For example, the techniques of decomposition by combustion with or without oxygen gas at high temperatures [2,3], vitrification [4], oxidative treatment using supercritical water [5,6], and dehalogenation by hydroxide using KOH in DMI (1,3-dimethyl-2-imidazolidinone) with heating [7,8], seemed to present some success for detoxification. However, these methods, which involve high temperature and/or high pressure conditions, have some disadvantages in recovering the vaporized dioxins and PCBs, in driving up operating costs, and in incurring the high risk of de novo synthesis of dioxins. On the other hand, a few methods using mild conditions, such as an alkali metal like metallic sodium in oil [9], bioremediation method [10] and mechano-chemical systems by energy emissions from collision between metallic small balls

[11] were proposed. However, these methods also present some unfavorable aspects concerning the use of dangerous reducing reagents such as metallic sodium, low decomposition rates, output, or efficiency.

Dechlorination is an effective alternative procedure for decomposing chlorinated organic wastes under relatively mild conditions without the formation of the toxic by-products [12,13].

Catalytic dechlorination with noble metal and transition metal catalysts is an especially simple and efficient method. Molecular hydrogen is often used as a hydrogen source in the catalytic dechlorination. Hydrogen-transferring reactions using hydrogen donors such as alcohols and formats have also been studied extensively [14].

In recent years, catalytic dechlorination methods have been developed including transfer hydrogenation by means of hydrogen donors such as metal hydrides [15], formic acid and its salts and alcohols [16,17], which use water or methanol as solvents. The practical application of catalysts to the dechlorination of organic halides is always accompanied by the problem of deactivation of the catalyst [18]. It is well known that both halogenation and dehalogenation reactions are also catalyzed by municipal waste incinerator (MWI) fly ash at elevated temperatures and proceed simultaneously on the flyash surface [19–23]. Hagenmaier et al. demonstrated that, under oxygen deficiency, the destruction of PCDD, PCDF and other chlorinated aromatics is a general property of flyash from waste incineration processes [24,25]. The authors have proved that dechlorination/hydrogenation of PCDD/PCDF and

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other chlorinated aromatic compounds on fly ash are catalyzed under certain conditions [26]. This catalytic property of flyash is being applied for low temperature decontamination of flyash during industrial scale operations [27,28].

The present study was focused on dechlorination of simulated solutions of the chlorinated aromatic compounds by using flyash and applying reducing agents under mild conditions. The effect of metals [29–32], water [33,34] and organic solvents acting as hydrogen donors [18–37] on dechlorination of chlorobenzene compounds has been reported by different authors. We also tested the effects of water/organic solvents, temperatures, metals and heating time on dechlorination and reactions conditions were optimized to get maximum dechlorination.

2. Experimental

The dioxins-free fly ash was taken from the local municipal waste incinerator and its metallic composition was analyzed by acid digestion method. The digestion methodology to analyze metals was based on the USEPA method 3051A (1998). About 0.5 g fly ash sample was digested with 9 ml concentrated nitric acid and 3 ml concentrated hydrochloric acid in a microwave sample preparation system (multiwave 3000, Anton Paar GmbH, Austria). Digested flyash sample was filtered by syringe membrane filter (0.45 μm) and diluted to 100 ml by adding double distilled water. Prepared sample was kept in polypropylene bottles (soaked in acid and washed with double distilled water prior to use).

The clear supernatant solution was analyzed for different metals. Most of the metals were analyzed using an Inductively Coupled Plasma Optical Emission Spectroscopy (PerkinElmer Optima 3100 RL) for Al (45 ppb), Cd (3 ppb), Cr (7 ppb), Cu (5 ppb), Fe (4 ppb), Pb (42 ppb), Mn (1 ppb), Sr (103 ppb) and Zn (1 ppb). As (2 ppb) and Sn (2 ppb) were determined by a polarized Zeeman Atomic Absorption Spectrophotometer (Graphite Furnace Atomizer, Hitachi Z-2000) by adding Pd/Mg mixture (concentration 500 ppm) to the sample solution in acidic medium. Hg (1 ppt) was determined by a cold vapor Atomic Absorption Spectroscopy (Hiranuma Mercury Analyzer, HG-310). The values given in parentheses are detection limits of each metal in ppb. The metallic composition of flyash is given in Table 1. Calcium hydroxide and sulfur was received as industrial chemical material (>99 %). Chlorinated aromatic compounds and organic solvents were received from Wako Pure Chemicals Industries Ltd.

3. Apparatus and procedures

The experiments were carried out in a mini reactor (MS-100C) equipped with reaction vessel (100 ml, 5 MPa), mini agitator

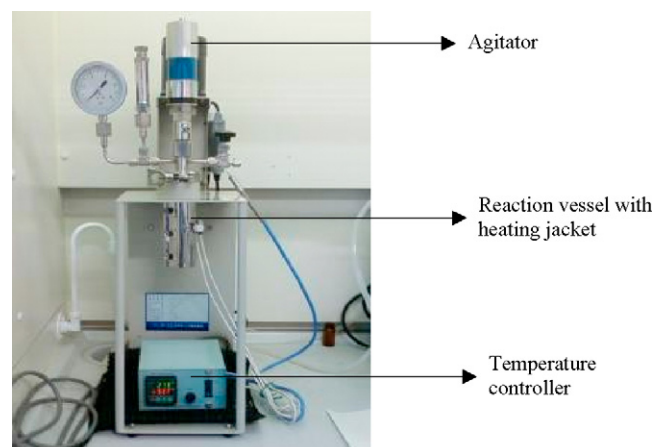


Fig. 1. Mini reactor (MS-100C).

(90–1500 rpm), electric heating jacket with digital temperature controller (200 °C max.) as shown in Fig. 1.

The experiments were carried out by using chlorinated benzene compounds. The simulated solutions of chlorinated aromatic compounds were mixed with flyash, sulfur and calcium hydroxide and agitated (250 rpm) at different temperatures for different durations in aqueous/organic solvent mixtures.

The experimental products were extracted twice with ether with total final volume of 20–30 ml. Combined organic layers were washed, dried on MgSO_4 then concentrated by evaporation to 5 ml volume. Dehalogenation products were analyzed using a gas chromatogram (HP 5890; Hewlett Packard series II) with internal standard (1-chloro-2,4-dinitrobenzene) for quantitative determina-

Table 2

Dechlorination of chlorobenzene (flyash (4 g); calcium hydroxide (2 g), sulfur (4 g), heating for 13 h)

Temperature (°C)	Yield (%)	
	$\text{C}_6\text{H}_4(\text{OH})\text{Cl}$	$\text{C}_6\text{H}_4\text{Cl}_2$
2.1. Water/methanol solvent 15/5 ml		
40	–	–
50	10	
60	25	
70	38	
80	47	
90	49	
120	30	10
150	22	25
170	18	38
2.2. Water/ethanol solvent 15/5 ml		
40	–	–
50	12	
60	45	
70	52	
80	58	
90	61	
120	38	15
150	35	20
170	20	25
2.3. Water/isopropanol solvent 15/5 ml		
40	–	–
50	15	
60	35	
70	60	
80	62	
90	68	
120	38	20
150	30	30
170	25	38

Table 1

Concentration of metals in flyash

Metals	Concentration (mg/kg)
Al	3670
As	2.8
Ba	105
Cd	39.5
Co	11
Cr	53.5
Cu	452
Fe	6340
Mn	453
Pb	1200
Sn	4.95
Sr	157
Zn	3730

Table 3

Dechlorination of di-chlorobenzene (flyash (4 g); calcium hydroxide (2 g), sulfur (4 g), heating for 13 h)

Temperature (°C)	Yield (%)					
	C ₆ H ₄ Cl ₂	C ₆ H ₅ Cl	C ₆ H ₄ (OH)Cl	C ₆ H ₄ (SH)Cl	C ₆ H ₃ Cl ₃	Dechlorination
3.1. Water/methanol solvent 15/5 ml						
60	75	20	5			12
70	60	30	10			20
80	40	40	10	10		30
90	20	50	20	10		37
120	28	45	5	5	17	19
150	35	45			20	12
170	30	45			25	10
3.2. Water/ethanol solvent 15/5 ml						
60	60	35	5			20
70	50	35	15			25
80	35	45	20			32
90	20	60	10	10		40
120	25	50	5	5	15	22
150	30	50			20	15
170	30	45			25	10
3.3. Water/isopropanol solvent 15/5 ml						
60	55	35	10			22
70	45	30	25			27
80	15	65	20			42
90	12	68	10	10		44
120	20	55	5	5	15	25
150	25	55			20	17
170	30	50			20	15

tion, equipped with DB-5 m column (30 m × 0.25 mm × 1 μm) and a quadrupole mass spectrometer (JEOL). Ionization was performed under 70 eV electron impact conditions (300 μA, 400 V) where the temperature initially was 35 °C, ramped at 15 °C/min to 150 °C and then at 3 °C/min to 280 °C.

A series of experiments were performed to optimize the concentration of flyash, calcium hydroxide and sulfur, water/organic solvent volume ratios and heating time. It was found that higher

dechlorination % was obtained with 4 g flyash, 2 g calcium hydroxide and 4 g sulfur in water/organic solvent (v/v, 3:1). Reaction mixtures for dechlorination of chlorobenzene compounds were heated at different temperatures from 2–17 h. Experimental results suggested that the dechlorination was increased by increasing the heating time and the maximum dechlorination percentage was achieved by heating for 13 h and heating for more than 13 h did not change the dechlorination results. In this paper

Table 4

Dechlorination of tri-chlorobenzene (flyash (4 g); calcium hydroxide (2 g), sulfur (4 g), heating for 13 h)

Temperature (°C)	Yield (%)						Dechlorination
	C ₆ H ₃ Cl ₃	C ₆ Cl ₆	C ₆ H ₅ Cl	C ₆ H ₄ (OH)Cl	C ₆ H ₄ Cl ₂	C ₆ HCl ₅	
4.1. Water/methanol solvent 15/5 ml							
60	72		25	3			18
70	46		32	10	12		36
80	18		50	12	20		48
90	15		60	10	15		51
120	30		49		16	5	34
130	25	10	45		15	5	22
150	30	15	35		15	5	10
170	30	18	32		15	5	5
4.2. Water/ethanol solvent 15/5 ml							
60	67		30	3			22
70	45		35	10	10		33
80	16		50	10	24		48
90	9		70	4	16		55
120	25		60		10	5	40
130	20	10	50		15	5	25
150	25	12	43		10	10	13
170	30	15	35		10	10	5
4.3. Water/isopropanol solvent 15/5 ml							
60	40		35	10	15		35
70	27		42	13	18		43
80	11		61	16	12		55
90	5		70	15	10		60
120	10		54		30	6	42
130	10	10	50		25	5	28
150	15	15	40		25	5	16
170	20	15	40		15	10	10

Table 5

Dechlorination of hexa-chlorobenzene (flyash (4 g); calcium hydroxide (2 g), sulfur (4 g), heating for 13 h)

Temperature (°C)	Yield (%)						Dechlorination
	C ₆ Cl ₆	C ₆ HCl ₅	C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₃	C ₆ H ₄ (OH)Cl	C ₆ H ₅ Cl	
5.1. Water/methanol solvent 15/5 ml							
60	70		10		5	15	23
70	55		15	5	5	20	35
80	38		18	7	15	22	46
90	30		15	5	10	40	54
120	35	5	15	10		35	45
130	40	8	12	10		30	39
150	45	15	10	10		20	31
170	50	10	15	15		10	27
5.2. Water/ethanol solvent 15/5 ml							
60	65		10		10	15	27
70	45		20		10	25	42
80	30		15		20	35	56
90	17		13	5	10	55	65
120	23	7	10	10		50	58
130	25	10	10	15		40	49
150	31	12	10	15		32	42
170	35	15	12	18		20	39
5.3. Water/isopropanol solvent 15/5 ml							
60	50		20		10	20	38
70	40		15		10	35	47
80	20		10		12	58	65
90	10		8		15	67	74
120	20	5	15	10		50	62
130	25	10	15	12		38	49
150	30	10	15	15		30	44
170	35	10	10	20		25	39

Table 6

Dechlorination of di-chlorobenzene in presence of metals as additives (flyash (4 g); calcium hydroxide (2 g), sulfur (4 g), water/isopropanol; 15/5 mL, heating for 13 h)

Additives (metals)	Temperature (°C)	Yield (%)					Dechlorination
		C ₆ H ₄ Cl ₂	C ₆ H ₅ Cl	C ₆ H ₄ (OH)Cl	C ₆ H ₄ (SH)Cl	C ₆ H ₃ Cl ₃	
Fe	90	10	65	15	10		45
Cu	90	5	80	10	5		47
Mn	90	10	70	10	10		45
Pb	90	8	72	10	10		46
Zn	90	10	65	10	15		45
Al	90	10	65	15	10		45
Fe	120	15	70			15	27
Cu	120	10	65			25	20
Mn	120	15	65			20	22
Pb	120	20	60			20	20
Zn	120	20	65			15	25
Al	120	25	60			15	22
Fe	150	15	60			25	17
Cu	150	20	50			30	10
Mn	150	20	55			25	15
Pb	150	15	55			30	12
Zn	150	15	60			25	17
Al	150	20	55			25	15

Metals added: Fe (15.9 mmol); Cu (15.9 mmol); Mn (18.2 mmol); Pb (4.8 mmol); Zn (15.4 mmol); Al (18.5 mmol).

experimental results with heating time of 13 h (optimum time) were mentioned and discussed.

Experimental yields (amount of products obtained in experiments) are presented in Tables 2–6, in which the contents of chloro-compounds substrates and dechlorinated products are expressed in wt.% and the extent of dechlorination is expressed as the percent of chlorine lost by dechlorination relative to the original chlorine contents in the substrates by following formula:

$$\text{Dechlorination}(\%) = \left(C_s - \frac{C_p}{C_s} \right) \times 100$$

where C_s and C_p denote the chlorine contents in substrate and products, respectively.

4. Results

4.1. Dechlorination of chlorobenzene

A simulated solution of chlorobenzene (0.25 mol dm⁻³) was mixed with flyash (4 g), calcium hydroxide (2 g) and sulfur (4 g) in the mixture of water and organic solvent. The reaction mixture was agitated at 40–170 °C, for 13 h in an air sealed reaction vessel and

products were extracted with ether and analyzed on GC/MS. The results showed that final products of chlorobenzene were chlorophenol and dichlorophenol. The change in temperature changed the % of chlorophenol and it was highest at 90 °C, as shown in Table 2. The yield of chlorophenol was higher in water/isopropanol mixture (Table 2.3) as compared to water/ethanol (Table 2.2) and water/methanol mixture (Table 2.1). At temperatures from 50 to 90 °C, the yield was only chlorophenol whereas at higher temperatures (120–170 °C), di-chlorobenzene was produced along with chlorophenol.

4.2. Dechlorination of di-chlorobenzene

A simulated solution of di-chlorobenzene (0.25 mol dm^{-3}) was treated with flyash (4 g), calcium hydroxide (2 g) and sulfur (4 g) in the mixture of water and organic solvent at 60–170 °C for 13 h and results were given in Table 3. Maximum dechlorination was observed at 90 °C, in water/isopropanol mixture as compared to water/ethanol and water/methanol mixture. At lower temperatures 60–90 °C, chlorobenzene, 2-chlorophenol and chlorobenzene thiol was produced but at higher temperatures (120–170 °C), 1,3,5 tri-chlorobenzene was produced.

4.3. Dechlorination of tri-chlorobenzene

Dechlorination of tri-chlorobenzene (0.25 mol dm^{-3}) was carried out under above said optimized reaction conditions and results were given in Table 4. Dechlorination was higher at 90 °C, in water/isopropanol mixture as compared to water/ethanol and water/methanol mixture. The consequential products at 60–90 °C, were chlorobenzene, 2-chlorophenol and 1,3-dichlorobenzene whereas, at 120–170 °C, penta-chloro and hexa-chlorobenzene were produced besides these products.

4.4. Dechlorination of hexa-chlorobenzene

Dechlorination of hexa-chlorobenzene (0.25 mol dm^{-3}) was carried out by using flyash (4 g), calcium hydroxide (2 g) and sulfur (4 g) in the mixture of water and organic solvent and heated at 60–170 °C, for 13 h. The dechlorination was higher at 90 °C, in water/isopropanol mixture as compared to water/ethanol and water/methanol mixture. At 60–90 °C, dechlorination products were chlorobenzene, 2-chlorophenol, and 1,3,5 tri-chlorobenzene whereas, at 120–170 °C, penta-chlorobenzene was produced besides these products.

In general, under optimized reaction conditions the dechlorination % of hexa-chlorobenzene was higher than tri-chlorobenzene and di-chlorobenzene as shown in Fig. 2.

4.5. Effect of metals on dechlorination

The effect of metals [6–8], metals oxides [9], water [3] and organic solvents acting as hydrogen donors [8] on dehalogenation of organohalogen compounds has been reported by different authors.

To study the effect of metals on the course of dechlorination, di-chlorobenzene (0.25 mol dm^{-3}) was treated with flyash (4 g), calcium hydroxide (2 g) and sulfur (4 g) in the mixture of water and isopropanol solvent at 90–150 °C, for 13 h (optimized reaction conditions). The main metals of flyash, Fe (15.9 mmol); Cu (15.9 mmol); Mn (18.2 mmol); Pb (4.8 mmol); Zn (15.4 mmol); Al (18.5 mmol) were added in the reaction mixtures. Results (Table 6) revealed that these metals in general and copper and lead in particular affect positively at 90 °C, as compared to experiments without additives. But at temperatures 120–170 °C, these metals in

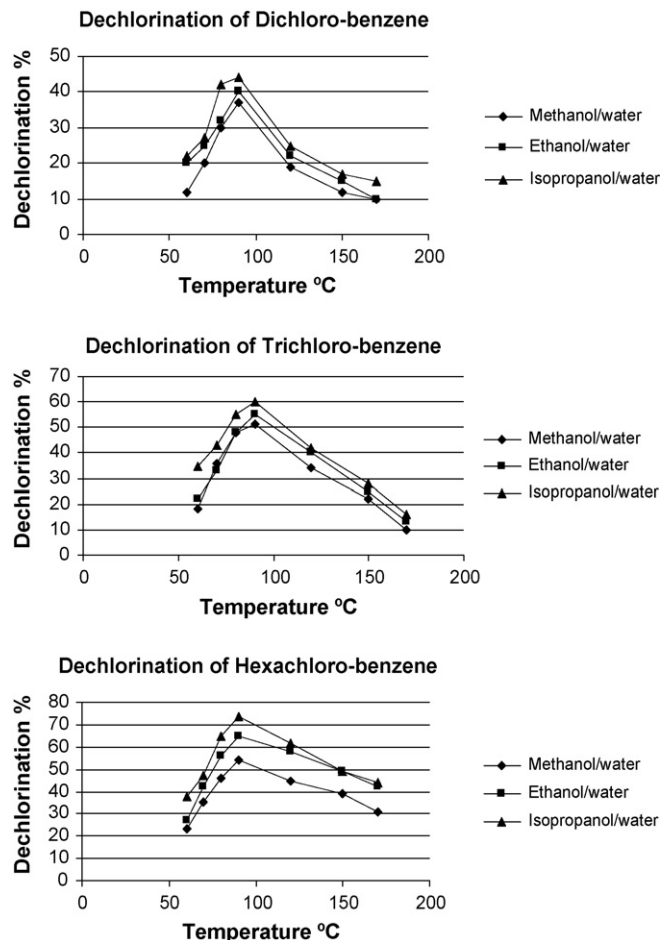


Fig. 2. Dechlorination of chlorobenzene compounds.

general and copper and lead in particular adversely affected the dechlorination process as compared to experiments without them; prevailing dechlorination products being chlorobenzene, 2-chlorophenol, chlorobenzene thiol and 1,3,5 tri-chlorobenzene as shown in Table 6.

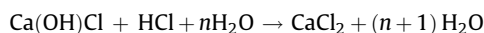
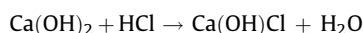
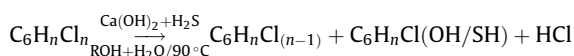
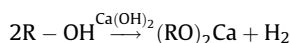
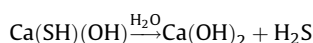
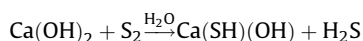
5. Discussion

Results demonstrate that the dechlorination percentage was maximum in isopropanol solvent as reported by Concibido et al. [39] in the order as: isopropanol > ethanol > methanol. An increase in the percentage of dechlorination in isopropanol clearly suggests that organic solvent functions as a hydrogen-donor in the catalytic hydrodechlorination of chlorobenzene compounds. It is assumed that the catalytic dechlorination of chlorobenzenes in solution of calcium hydroxide and sulfur in isopropanol involved hydrogen transfer from organic solvent to the aromatic chlorines and displaces a chloride anion from the ring of chlorobenzenes, as suggested by Ukisu et al. [42]. Thus we concluded that organic solvents act as hydrogen donors more than to dissolve the organic compounds in reaction media, as observed by others researchers [2,33,18–37,41].

Maximum dechlorination was obtained when a relatively high v/v ratio of water with isopropanol (3:1) was used. The enhancement in the dechlorination in excess of water [38–40] presumed to arise from controlling the solubility of substrate, the additives and the products other than hydrogen source as reported by Ukisu et al. [41]. This argument was supported by the work of

other authors [35,36] who use metals in alcohols to reduce the chlorinated compounds in the absence of water.

Furthermore, the formation of chlorophenol and chlorothiophenol suggested that reaction mixture has free hydroxyl and hydrosulfide ions that substitute the chloride ions of chlorobenzene congeners under specified conditions. Based on dechlorination results a mechanism was postulated that calcium hydroxide and sulfur react to produce calcium polysulfide which in the presence of water decomposed to provide a mixture of $\text{Ca}(\text{SH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{SH})(\text{OH})$. In the presence of water $\text{Ca}(\text{SH})(\text{OH})$ further produces $\text{Ca}(\text{OH})_2$ and H_2S , where H_2S acts as a strong reducing agent to reduce chlorinated compounds. In addition, on the aromatic ring chlorine is substituted by the hydrogen from the hydroxyl group of the alcohol and the alkoxide ions quenched by the Ca^{2+} cations. Calcium hydroxide also neutralized the resultant HCl in the reaction mixture.



OH^- and SH^- ions act as nucleophilic and the reaction has been assumed to proceed as a nucleophilic substitution. Due to relatively electron withdrawing effect of chlorine atoms the first nucleophilic attack should be easier for polychlorinated isomers as the greater number of chlorine atoms present on the nucleus will weaken the C–Cl bond. This assumption was confirmed by the relative high dechlorination % of hexa-chlorobenzene than tri-chlorobenzene and di-chlorobenzene.

Under optimized conditions dechlorination was substantially increased with increase in temperature and it was the maximum at 90°C . But when reaction mixture was heated at more than 90°C , dechlorination decreased with increase in temperature and further chlorination occurred. At 120 – 170°C , tri-chlorobenzene was produced during the dechlorination of di-chlorobenzene and hexa-chlorobenzene was produced during dechlorination of tri-chlorobenzene. These results revealed that under high temperature further chlorination was carried out under same reaction conditions. This phenomenon led us to assume that metals of flyash might have different role at different temperatures.

Results (Table 6) described that at 90°C , dechlorination percentage was increased by adding metals where copper and lead were found to catalyze dechlorination process more than other metals [30,31,33]. But at 120 – 150°C , dechlorination was decreased by adding the metals particularly copper and lead. This phenomenon suggests that metals in general and copper and lead in particular have adverse effect on dechlorination and these metals can catalyze the further chlorination process at higher temperature.

Low percentage of dechlorination and/or further chlorination at higher temperatures postulated that at high temperatures (120 – 170°C), water and alcohol solvent existed in vapor phase that suppressed the H_2S gas and decreased the concentration of OH^- and SH^- ions to substitute chloride ions and the Cl^- ions present in the reaction mixture caused further chlorination, and metals at high temperature act as catalysts to perform further chlorination on the surface of flyash as observed by other authors [31,33,41,42].

6. Conclusion

It is conceivable that fly ash is a remarkable substrate to catalyze the dechlorination processes. Flyash in the presence of calcium hydroxide and sulfur in water/isopropanol solution at 90°C , under oxygen deficient conditions can catalyze the dechlorination of chlorinated aromatic compounds. Dechlorination efficiency was enhanced by adding metals at 90°C . At low temperature catalytic effect of flyash can be ascribed to the effect of metals but the catalytic effect of these metals was adverse at high temperature. Besides the metals, reducing agent with hydrogen donor (isopropanol) and water is necessary to carry out dechlorination process by flyash. In this study, from global point of view, solid waste (flyash) was utilized for dechlorination/or detoxification of simulated solutions of most hazardous chlorobenzene compounds by adding reducing agents (calcium hydroxide and sulfur) and dechlorination percentage of 44–47%, 60% and 74% for di-chlorobenzene (0.25 mol dm^{-3}), tri-chlorobenzene (0.25 mol dm^{-3}) and hexa-chlorobenzene (0.25 mol dm^{-3}), respectively, was achieved by optimizing the reaction conditions (temperature, heating time, water/organic solvent volume ratios). Furthermore, these mild conditions are acquirable on industrial scale to dechlorinate and/or detoxify the chlorobenzene liquid and/or solid wastes as well.

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